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(54) FUNCTIONAL MATERIAL, OXIDIZING CATALYST, COMBUSTION CATALYST,
METHANOL MODIFIED CATALYST AND ELECTRODE CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a functional material of superior function of absorbing oxygen under the oxidizing atmosphere and exhaust oxygen under the reduction atmosphere by using an element of specified value in a cerium oxide represented by the specified formula.

SOLUTION: A function material is represented by the formula of $(A_xCe_{1-x})O_2$ (In the formula, A represents at least one element selected out of a group Y, Sc and lanthanoid, and $0.1 < X < 1$). The value of X in the formula is set preferably in the range of approximately 0.2-0.7, more preferably approximately 0.3-0.7 (both included). As the particle diameter of the functional material, approximately 0.01-100 μ m is preferred. The functional material of superior capability of absorbing oxygen under the oxidizing atmosphere and existing oxygen under the oxidizing atmosphere can be provided by the above arrangement, and also an oxidizing catalyst, a combustion catalyst, a methanol modified catalyst and an electrode catalyst of high catalyst activities and superior continuity of catalyst activities for achieving the efficient utilization of energy resources and the reduction of generation of environmental pollutants can be provided by the application of the above arrangement.

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CLAIMS

[Claim(s)]

[Claim 1] Chemical formula: $(A xCe_{1-x})$ The functional material expressed with O₂ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$).

[Claim 2] Chemical formula: $(A xCe_{1-x})$ The oxidation catalyst characterized by providing the functional material expressed with O₂ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$).

[Claim 3] Chemical formula: $(A xCe_{1-x})$ The oxidation catalyst characterized by providing at least one sort of matter chosen from the group which consists of a functional material expressed with O₂ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), and a compound containing a noble-metals element and a noble-metals element.

[Claim 4] Chemical formula: $(A xCe_{1-x})$ The combustion catalyst characterized by providing at least one sort of matter chosen from the group which consists of a functional material expressed with O₂ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), and a compound containing a noble-metals element and a noble-metals element.

[Claim 5] Chemical formula: $(A xCe_{1-x})$ The methanol reforming catalyst characterized by providing at least one sort of matter chosen from the group which consists of a functional material expressed with O₂ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), and a compound containing a noble-metals element and a noble-metals element.

[Claim 6] Chemical formula: $(A xCe_{1-x})$ The electrode catalyst characterized by providing at least one sort of matter chosen from the group which consists of a functional material expressed with O₂ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), and a compound containing a noble-metals element and a noble-metals element.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the electrode catalyst used for the oxidation catalyst which realized high catalytic activity, a combustion catalyst, the reforming catalyst of a methanol, a solid oxide fuel cell, etc. by using the functional material which is excellent also in the capacity which emits the absorbed oxygen, and this functional material while it is excellent in the capacity which absorbs oxygen.

[0002]

[Description of the Prior Art] In recent years, exhaustion-izing of the energy resource represented by fossil fuels, such as petroleum and coal, and the increment in the environmental pollutant generated in case energy is taken out from a fossil fuel serve as a big social problem. That is, exhaustion-ization of the energy resource represented by the fossil fuel influences human beings' activity directly in the present condition that the leading energy source replaced with a fossil fuel is not developed. Moreover, the increment in an environmental pollutant brings about destruction of the ecosystem of a terrestrial scale, and makes dangerous not only human beings but existence of the versatility of a seed. Therefore, it is indispensable it to be a problem of the utmost importance from from [when divining the future earth] to control exhaustion-ization of an energy resource, to control generating of an environmental pollutant, and to maintain an ecosystem, to use an energy resource efficiently for that purpose, and to reduce an environmental pollutant.

[0003] Then, in order to fill an above-mentioned demand, with the gas turbine which uses natural gas and generates electricity efficient, the emission-gas-purification catalyst which defecates the exhaust gas of an automobile, the reaction catalyst which generates a product with a high invert ratio, and high conversion efficiency, means, such as a fuel cell which generates electrical energy, are at a quick pace, and are developed. Although various ingredients are proposed according to the spec. demanded from current and these means, the stability of a cerium compound in the inside of an operating environment is high especially, oxygen is absorbed under an oxidizing atmosphere, and it is widely used as an important ingredient from having the property of emitting oxygen under reducing atmosphere.

[0004] Although it is becoming in use to burn the fuel which uses methane etc. as a principal component by oxidation reaction therefore, the palladium which starts oxidation reaction from whenever [low-temperature] is used for a gas turbine as a catalyst component in many cases. By the way, palladium has the property that catalytic activity is low when catalytic activity is high at the time of an oxidation state (PdO) and it is a metal (Pd). According to the balance governed by oxygen tension and ambient temperature, oxidization palladium emits oxygen above 900 degrees C, and serves as a metal (Pd).

[0005] It is the redox reaction which the catalytic reaction of the combustion catalyst which uses oxidation palladium as a catalyst component generally oxidizes in hydrocarbons in the state of the oxide of Pd-O in which oxygen carried out the dissociative adsorption to the catalyst front face, and it is returned and oxidization palladium itself serves as a metal (Pd), and a metal (Pd) oxidizes again, generates the oxide condition of Pd-O, repeats this, and oxidizes in hydrocarbons. In oxidation reaction of the usual hydrocarbons, since there is not much reacting weight, a redox cycle advances smoothly on a catalyst front face. However, like a gas turbine, by the system of reaction with the

large calorific capacity of combustion chamber (the amount of oxidation reaction), while the oxygen of Pd-O which the balance of a redox cycle collapsed and carried out the dissociative adsorption to the catalyst front face is consumed easily, the oxygen of the oxidation palladium (PdO) of the bulk which exists inside a combustion catalyst is considered to move to a catalyst front face and to be used for oxidation of a fuel. That is, in the initial state of oxidation reaction, since most palladium in a combustion catalyst is oxidation palladium, high catalytic activity is presented, but since the oxygen of the oxidation palladium (PdO) of bulk is consumed with advance of a combustion reaction, a metal (Pd) rate increases to a catalyst front face, and catalytic activity falls. Then, to maintain the catalytic activity of a combustion catalyst is tried by making the cerium oxide which the oxygen in an ambient atmosphere is absorbed under an oxidizing atmosphere, and can emit oxygen under reducing atmosphere live together with palladium.

[0006] Moreover, although the three way component catalyst which consists of Pt, Pd, and Rh is used as an emission-gas-purification catalyst in order to reduce the concentration of the hydrocarbon in exhaust gas, a carbon monoxide, or nitrogen oxides, without spoiling an engine performance and fuel consumption, to add cerium oxide to this three way component catalyst is tried. That is, by demonstrating the co-catalyst effectiveness of cerium oxide, while reducing the amount of the noble metals used in a three way component catalyst, oxygen tends to be absorbed under an oxidizing atmosphere and it is going to correspond to fluctuation of the air-fuel ratio resulting from the transit mode of an automobile with the property of the cerium oxide which can emit oxygen under reducing atmosphere.

[0007] Furthermore, on the occasion of the reforming reaction of a methanol, $O(Nd \ xCe \ 1-x) \ 2$ etc. is used as a reaction catalyst which promotes oxidation reaction ($0 \leq x \leq 0.1$).

[0008] Moreover, in the solid acid ghost electrolyte mold fuel cell, as a positive-electrode catalyst, it is stable in 1000-degree C air, and the porous body of electronic conductivity represented by the perovskite mold lanthanum system transition-metals oxide of air and the structure which has large contact with electrolytic both is used.

[0009]

[Problem(s) to be Solved by the Invention] However, in conventional cerium oxide or perovskite mold lanthanum system transition-metals oxide, there was a problem that the capacity which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere was low.

[0010] Moreover, since neither conventional cerium oxide nor perovskite mold lanthanum system transition-metals oxide was enough as the capacity which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere, and the catalytic activity of the catalyst which applied these did not fully go up and it became scarce also at the durability of catalytic activity, there was a problem that where of it was difficult to attain current, efficient use of the energy resource demanded, and reduction of an environmental pollutant.

[0011] This invention aims at offering the functional material which is excellent in the capacity which was made in order to solve the above-mentioned problem, absorbs oxygen under an oxidizing atmosphere, and emits oxygen under reducing atmosphere.

[0012] Moreover, catalytic activity of this invention is high, and it excels also in the durability of catalytic activity, and aims at offering the oxidation catalyst which attains efficient use of an energy resource, and reduction of an environmental pollutant, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst.

[0013]

[Means for Solving the Problem] In the cerium oxide by which this invention persons are expressed with chemical formula: $(A \ xCe \ 1-x) \ O_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula) By making the value of x in the rate, i.e., above-mentioned chemical formula, of Element alpha increase from 0.1, oxygen is absorbed under an oxidizing atmosphere, and it finds out that the engine performance which emits oxygen under reducing atmosphere improves by leaps and bounds, and results in this invention.

[0014] That is, the functional material concerning this invention is characterized by what is expressed with chemical formula: $(A \ xCe \ 1-x) \ O_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$).

[0015] In the functional material of this invention, since electronic conductivity is high, the oxygen

in an oxidizing atmosphere is easily dissociated by the following reactions, and it is thought that it is incorporated to the hole which exists in a functional material.

[0016] $1/2O_2 + (\text{inside of gaseous phase})2e^- \rightarrow (\text{functional material}) O_2 - (\text{hole})$

On the other hand, under reducing atmosphere, it is thought that the oxygen (ion) incorporated in the hole is easily emitted to the exterior of a functional material by the following reactions.

[0017] $O_2 - (\text{hole}) \rightarrow 1/2O_2 + (\text{inside of gaseous phase})2e^- - (\text{functional material})$

As mentioned above, it is thought that the functional material of this invention excels [conductivity] in the capacity which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere since electronic conductivity is high. The functional material of this invention has the property of specific resistance 100 ohm-cm extent at 400 degrees C.

[0018] What is necessary is just to set the value of x in the rate, i.e., above-mentioned chemical formula, of Element alpha as the range of 0.1-1 (however, for an endpoint not to be included) in the functional material of this invention, in order to make the engine performance which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere discover good.

However, fitness can be made to discover more the engine performance which absorbs oxygen for the value of x in the above-mentioned chemical formula under an oxidizing atmosphere by 0.2 to 0.7, and setting it as the range of 0.3-0.7 (an endpoint being included) more preferably, and emits oxygen under reducing atmosphere.

[0019] Moreover, if in charge of manufacturing the functional material concerning this invention, it is desirable to dope Element alpha to Seria (CeO₂) using a coprecipitation method. Although it is about 0.01-100 micrometers preferably as a particle size of the particle of a functional material, it is more desirable when it is made about 0.1-10 micrometers. Furthermore, in order to make the engine performance which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere discover good, it is desirable to, enlarge surface area of a functional material if possible, and to make the place of a reaction increase. If the surface area of a functional material is 1-100 [m² / g] extent in BET surface area, the engine performance which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere can be made to discover good practical.

[0020] In addition, as it is indicated in drawing 4 as the particle size of a particle, the diameter d at the time of converting the particle of the functional material of the configuration of arbitration recognized two-dimensional, 8 [for example,], into the virtual particle 9 expressed two-dimensional shall be pointed out. That is, it asks for the area of the particle 8 of the functional material of the configuration of arbitration. Next, it asks for the circular virtual particle 9 which has an area equal to the called-for area, and let the diameter d of a virtual particle 9 be the particle size of a functional material 8. The particle size of the particle of the functional material mentioned above is the value calculated from the virtual particle 9. Moreover, mean particle diameter is a value equivalent to the average of the particle size obtained based on the particle size of each functional material in the aggregate of a functional material. Henceforth, the particle size and mean particle diameter of the matter shall be given by the numeric value computed according to the definition mentioned above.

[0021] Next, the oxidation catalyst concerning this invention is characterized by providing the functional material expressed with chemical formula: $(A xCe_{1-x}) O_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$).

[0022] Moreover, the functional material by which the oxidation catalyst concerning this invention is expressed with chemical formula: $(A xCe_{1-x}) O_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), It is characterized by providing at least one sort of matter chosen from the group which consists of a compound containing a noble-metals element and a noble-metals element.

[0023] Furthermore, the functional material by which the combustion catalyst concerning this invention is expressed with chemical formula: $(A xCe_{1-x}) O_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), It is characterized by providing at least one sort of matter chosen from the group which consists of a compound containing a noble-metals element and a noble-metals element.

[0024] Moreover, the methanol reforming catalyst concerning this invention is chemical formula: $(A$

$x\text{Ce } 1-x) \text{O}_2$ (among a formula). A is characterized by providing at least one sort of matter chosen from the group which consists of at least one sort of elements chosen from the group which consists of Y, Sc, and a lanthanoids and a functional material expressed with $0.1 < x < 1$, and a compound containing a noble-metals element and a noble-metals element.

[0025] Furthermore, the functional material by which the electrode catalyst concerning this invention is expressed with chemical formula: $(A \text{ } x\text{Ce } 1-x) \text{O}_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula, and $0.1 < x < 1$), It is characterized by providing at least one sort of matter chosen from the group which consists of a compound containing a noble-metals element and a noble-metals element.

[0026] In the oxidation catalyst concerning this invention, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst, the property of a functional material is as having mentioned above. Moreover, an oxidation catalyst, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst are extensive concepts which also name generically the base material possessing the compound containing the support which supported the compound containing the mixture, the functional material, noble-metals element, or noble-metals element of the compound containing a functional material, a noble-metals element, or a noble-metals element, and other additives, and the above-mentioned mixture, a functional material, a noble-metals element, or a noble-metals element, the above-mentioned mixture, or the above-mentioned support not to mention the compound containing a functional material, a noble-metals element, or a noble-metals element.

[0027] The oxidation catalyst, the combustion catalyst, methanol reforming catalyst, and electrode catalyst of this invention tend to be crowded for the functional matter in the oxygen which a chemical reaction takes, are emitting oxygen on the aspect of affairs which lacked oxygen in the reaction process, tend to cancel lack of the oxygen in a reaction process, and always tend to advance a chemical reaction smoothly.

[0028] In the oxidation catalyst of this invention, although a functional material may be used independently, in order to advance oxidation reaction more smoothly, it is more desirable to use together the compound containing a functional material, a noble-metals element, or a noble-metals element. In the oxidation catalyst, the combustion catalyst, methanol reforming catalyst, and electrode catalyst of this invention, a noble-metals element names generically gold, silver, and platinum group metals (Ru, Rh, Pd, Os, Ir, and Pt). Moreover, the compound containing a noble-metals element is an oxide of for example, a noble-metals element. About 0.01-100 micrometers of particle size of the particle of the compound containing a noble-metals element and a noble-metals element are more preferably set to about 0.1-10 micrometers.

[0029] Although it is different into how much a rate with the compound containing a functional material, a noble-metals element, or a noble-metals element is made with a catalyst system, it is specified about as follows. Namely, what is necessary is for the total quantity of the oxygen atom supplied to per unit time amount from a functional material at a noble-metals element to increase more than the amount of the oxygen atom consumed in process of a chemical reaction, or just to make it be tales doses. More preferably, it is chosen as 50 - 75 mass % extent, and becomes 40 to 90 mass [of the whole which generally consists a functional material of a compound containing a functional material, a noble-metals element, or a noble-metals element] %, and the compound with which the remainder contains a noble-metals element or a noble-metals element.

[0030] Moreover, it sets for the oxidation catalyst, the combustion catalyst, methanol reforming catalyst, and electrode catalyst of this invention. For components other than the compound containing a functional material, a noble-metals element, or a noble-metals element, as a co-catalyst Nickel, magnesium, titanium, vanadium, chromium, manganese, the rare earth (a scandium --) containing iron, cobalt, copper, zinc, molybdenum, and a lanthanoids An yttrium, a lanthanum, a cerium, PURASEOJIUMU, neodymium, a promethium, Samarium, europium, GADONIUMU, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, a ruthenium, or the oxide of these metals may be added. When nickel or its oxide is added especially, improvement in catalytic activity is large.

[0031] At this time, the rate with the compound and co-catalyst containing a functional material, a noble-metals element, or a noble-metals element Although especially limitation is not carried out since it is suitably set up by the catalyst system, generally 40 to 90 mass [of the whole which

consists a functional material of the compound and co-catalyst containing a functional material, a noble-metals element, or a noble-metals element] % -- more preferably ten to 60 mass [of the whole which consists of a functional material, a noble-metals element, and a co-catalyst the compound which chooses it as 50 - 75 mass % extent, and contains a noble-metals element or a noble-metals element] % -- it is more preferably chosen as 15 - 40 mass % extent. And the remainder serves as a co-catalyst. Moreover, about 0.01-100 micrometers is desirable still more desirable, and the mean particle diameter of a co-catalyst is about 0.1-10 micrometers.

[0032] Moreover, in the oxidation catalyst, the combustion catalyst, methanol reforming catalyst, and electrode catalyst of this invention, although it is also possible to use the compound containing a functional material or a functional material, a noble-metals element, or a noble-metals element as a catalyst with the gestalt of a particle, it is desirable to make other support support the particle of the compound containing a functional material or a functional material, a noble-metals element, or a noble-metals element preferably. Moreover, when a co-catalyst is added to the compound containing a functional material or a functional material, a noble-metals element, or a noble-metals element, it is desirable to make other support support these particles. When it is contributing to raising catalytic activity by the pore formed in the interior of oneself etc. and a catalyst bed is formed, support has the effectiveness which forms pore into a catalyst bed, while preventing the phenomenon which the compound and co-catalyst containing a functional material, a noble-metals element, or a noble-metals element condense on the occasion of the use as a catalyst.

[0033] As matter which constitutes support, ceramics, such as an oxide, a nitride, or carbide, is mentioned. Although it may react with the oxygen contained in an ambient atmosphere, the metal support itself may oxidize and it may finally become oxide support if a metal is made into support, what does not oxidize is usable as metal support. In these, since a metallic oxide, especially the oxide of a transition-metals element can serve as help which exchanges oxygen between a functional material or a noble-metals element, and raises catalytic activity, they are desirable. In oxide, a zirconia (ZrO_2) is desirable especially, and the cubic system zirconia which performed stabilization by yttria (Y_2O_3) further is desirable. Moreover, two or more kinds of mixed stock chosen from the above-mentioned matter is sufficient as support. Furthermore, a noble-metals element can also be supported by making the functional matter concerning this invention itself into support, and it is also possible not to use other matter as support.

[0034] 30 to 70 mass [of the whole which the rate of a functional material and support generally becomes from a functional material and support about a functional material although especially limitation is not carried out when supporting a functional material to support] % -- more preferably, it is chosen as 40 - 60 mass % extent, and let the remainder be support. When supporting the compound containing a functional material, a noble-metals element, or a noble-metals element to support, moreover, the rate with the compound and support containing a functional material, a noble-metals element, or a noble-metals element Although especially limitation is not carried out since it is suitably set up by the catalyst system, generally 30 to 60 mass [of the whole which consists a functional material of the compound and support containing a functional material, a noble-metals element, or a noble-metals element] % -- more preferably ten to 30 mass [of the whole which consists of the compound and support containing a functional material, a noble-metals element, or a noble-metals element the compound which chooses it as 40 - 60 mass % extent, and contains a noble-metals element or a noble-metals element] % -- it is more preferably chosen as 15 - 30 mass % extent. And let the remainder be support. Furthermore, when the compound and co-catalyst containing a functional material, a noble-metals element, or a noble-metals element are supported to support, The rate of the compound containing a functional material, a noble-metals element, or a noble-metals element, a co-catalyst, and support Although especially limitation is not carried out since it is suitably set up by the catalyst system, generally 30 to 60 mass [of the whole which consists a functional material of the compound, the co-catalyst, and support containing a functional material, a noble-metals element, or a noble-metals element] % -- more preferably ten to 30 mass [of the whole which consists of the compound, the co-catalyst, and support containing a functional material, a noble-metals element, or a noble-metals element the compound which chooses it as 40 - 60 mass % extent, and contains a noble-metals element or a noble-metals element] % -- it is more preferably chosen as 10 - 20 mass % extent. and five to 20 mass [of the whole which consists a co-

catalyst of the compound, the co-catalyst, and support containing a functional material, a noble-metals element, or a noble-metals element] % -- more preferably, it is chosen as 5 - 10 mass % extent, and let the remainder be support.

[0035] Although the distance with the compound and co-catalyst containing the compound containing a functional material, a noble-metals element, or a noble-metals element or a functional material, a noble-metals element, or a noble-metals element is so desirable that it is close when the compound and co-catalyst containing a functional material, a noble-metals element or a functional material, a noble-metals element, or a noble-metals element are supported to support, it does not need to be especially in contact. If distance with the compound and co-catalyst containing the compound containing a functional material, a noble-metals element, or a noble-metals element or a functional material, a noble-metals element, or a noble-metals element is about several nm, the property of a functional material will fully be demonstrated to the compound containing a noble-metals element or a noble-metals element.

[0036] As an approach of supporting the compound or co-catalyst containing a functional material, a noble-metals element, or a noble-metals element to support, the milling method, the sinking-in method, a coprecipitation method, or a spatter is mentioned. In order to make support (ceramics, such as an oxide, a nitride, or carbide) support the compound or co-catalyst containing a functional material, a noble-metals element, or a noble-metals element, it is also good to mix both powder, but since these interactions increase as a result of contact to the compound's, or the co-catalyst's and the heat-resistant matter's containing a functional material's, a noble-metals element's, or a noble-metals element becoming dense, and a touch area's also increasing and maintaining good contact, it is desirable to carry out milling using a ball mill. Especially ambient atmosphere conditions are not usually limited in the case of mixing. Moreover, it can obtain with the sinking-in method, plating, a spatter, a coprecipitation method, etc.

[0037] Moreover, when the compound or co-catalyst containing a functional material, a noble-metals element, or a noble-metals element is supported to support and it considers as powder, it is desirable to set average grain size of this powder to about 0.01-100 micrometers, but it is more desirable when about 0.1-10 micrometers. When the compound or co-catalyst containing a functional material, a noble-metals element, or a noble-metals element is supported to support and it considers as powder by the milling method, it is desirable to generate the secondary particle which a primary particle with a particle size of 0.01-1 micrometer or less condenses, and has the particle size of magnitude of this level.

[0038] In addition, in case a functional material or a functional material, and a noble-metals element are supported to support, when also supporting a co-catalyst, a co-catalyst may be added to coincidence at the time of mixing with support, and the compound and noble-metals element containing a functional material, a functional material, or a noble-metals element, and after mixing, you may add anew.

[0039] As mentioned above, the oxidation catalyst, the combustion catalyst, methanol reforming catalyst, and electrode catalyst of this invention tend to be crowded for the functional matter in the oxygen which a chemical reaction takes, are emitting oxygen on the aspect of affairs which lacked oxygen in the reaction process, tend to cancel lack of the oxygen in a reaction process, and always tend to advance a chemical reaction smoothly.

[0040] Here, the process of catalytic reaction is explained by making the combustion catalyst using palladium as a noble-metals element into an example. In addition, by supplying and compensating the oxygen equivalent to the amount taken from the oxidization palladium which is the high metallic oxide of catalytic activity at the time of combustion of a fuel out of a gaseous phase with the functional material with which it is easy to move oxygen ion, this combustion catalyst cancels the delay of the reoxidation rate of palladium, and always maintains, the high oxide condition, i.e., the oxidization palladium, of catalytic activity. That is, if oxygen is taken from oxidization palladium at a redox cycle reaction (combustion) at the time of combustion of a fuel, since oxygen will be supplied to the palladium which oxygen dissociated on the front face of the functional material which is supporting palladium, and lacked oxygen through the functional material, palladium is always maintained at the condition of the high oxidization palladium of catalytic activity, and catalytic activity is maintained over a long period of time.

[0041] Drawing 2 is what expanded a part of combustion catalyst 1 typically, and showed it, and it is the functional material which 2 supports oxidation palladium, and 3 supports oxidation palladium 2, and is functioning also as support. The interface whose 4 is a surface of action with the gaseous phase in which inflammable gas, such as a functional material 3, oxygen, and methane, exists, and 5 are interfaces which are the surfaces of action of oxidation palladium 2 and a functional material 3. And it is thought in four fields of the interior of the interface 4 shown in drawing 2, and a functional material 3, an interface 5, and oxidation palladium 2 that a reaction advances as follows.

[0042] (Interface 4) By the following reactions, oxygen is incorporated in the hole located in the interior of a functional material 3 from the inside of a gaseous phase.

[0043] $1/2O_2 + (\text{inside of gaseous phase})2e^- \rightarrow (\text{functional material 3}) O_2 - (\text{interior of a functional material 3})$

(Interior of the oxide support 3) In connection with advance of a combustion reaction at the oxidation palladium 2 which touched the interface 5 from the interface 4 to oxygen being incorporated, lack of oxygen is remarkable in the interior of a functional material 3. This lack serves as motive power and the oxygen incorporated from the interface 4 moves to an interface 5 from an interface 4 as oxygen ion.

[0044] (Interface 5) Lack of oxygen has become remarkable and oxygen ion is supplied by the following reactions from the interior of a functional material 3 to the palladium (oxidation) 2 of reduced condition.

[0045] $O_2 - (\text{interior of functional material 3}) + Pd(\text{oxidation}) (\text{palladium 2}) \rightarrow PdO(\text{oxidation palladium 2}) + 2e^- - (\text{functional material 3})$

PdO participates in a combustion reaction with methane again.

[0046] Through the reaction in the four above-mentioned fields, by performing supply of oxygen one by one to the palladium (oxidation) 2 of a gaseous phase a functional material 3 - reduced condition, the delay of the reoxidation rate of oxidation palladium 2 is canceled, and durability is obtained by the catalytic activity at the time of combustion.

[0047] In addition, although the reaction mechanism was explained with the functional material by making into an example the combustion catalyst which used palladium as a noble-metals element, in the oxidation catalyst concerning this invention, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst, the catalyst of the reaction is not carried out according to the same device, and it is not limited to this example especially as a gestalt of operation here.

[0048] As for the matter and co-catalyst which contain a functional material, a noble-metals element, or a noble-metals element in the oxidation catalyst concerning this invention, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst, it is desirable to use as powder, or to accept the need, although it is possible to use as powder which support was made to support as mentioned above, and to make these powder put and support on a base material. As a base material which makes these powder put and support, the honeycomb with which the plate, the pipe, the foam, the pellet, or opening of the product made from a heat-resistant ceramic or heat-resistant anti-oxidation metal was divided into the square, the rectangle, the triangle, or the hexagon is mentioned, for example. That is, like the base material 6 shown in drawing 3 with the catalyst for automobile exhaust, for example although processed into the configuration which suited the operating environment of a catalyst, a base material is about the honeycomb wall 7, in order to decrease a draft resistance more. It is constituted by about 0.1-0.5mm at the honeycomb structure made thin.

[0049] furthermore, like [in the case of using for the combustor of a gas turbine], in using it under a severe heat environment The quality of the material which has stability also in a high-temperature-oxidation nature ambient atmosphere since thermal resistance is required also of a base material, For example, although ceramics, such as an alumina, a silica, a magnesia, a corundum, a mullite, alpha-alumina, a zirconia spinel, and a titania, or stainless steel, Hastelloy, Inconel, other heat-resistant metals, etc. are mentioned When using it under a severe heat environment especially, it is effective to use Co radical heat-resistant alloy of nickel radical heat-resistant alloy of IN738, Mar-M247, and IN939 grade, FSX-414, HS-188, and MM509 grade.

[0050] In order to make the powder containing the matter containing a functional material, a noble-metals element, or a noble-metals element, or a co-catalyst, and the powder which made support support these powder put and support on a base material, the slurry containing these powder can be

created, and it can apply on a base material, and can carry out by [the] carrying out an afterbaking join. Moreover, when it is made to cover and support by ****(ing) the powder containing the matter containing a functional material, a noble-metals element, or a noble-metals element, or a co-catalyst, and support which made support support these powder to a base material, in order that base materials and these powder may join together firmly, since the catalyst which was excellent in abrasion resistance and peeling resistance under a harsh environment to which the gas of an elevated temperature and a high speed flows can be acquired, it is more desirable. As thermal spraying for forming a catalyst bed on a base material, various kinds of thermal-spraying approaches, such as a plasma metal spray method and an oxy-fuel-spraying method, are applicable. moreover, when a catalyst bed is formed by **** Since there is an inclination for the surface area of a catalyst bed to become small, add carbon material, such as graphite and polyester, to above-mentioned powder, and it considers as mixture. After carrying out thermal spraying of this mixture and forming a catalyst bed on a base material, since heat-treat a catalyst bed in an activated gas ambient atmosphere, many paths are formed in a catalyst bed in case carbon material will be removed from a catalyst bed, if processing which burns carbon material is performed, the surface area of a catalyst bed increases and catalytic activity becomes high, it is desirable.

[0051] Furthermore, in order to control exfoliation with a catalyst bed and a base material more, it is more desirable when the bond layer containing nickel, cobalt, iron, and at least one element of chromium is formed between a catalyst bed and a base material. If this bond layer is precise, it is good, and although especially a formation method is not limited, it is desirable, when it forms so that that consistency may be extent which gas does not penetrate substantially.

[0052] Moreover, it sets for the oxidation catalyst, the combustion catalyst, methanol reforming catalyst, and electrode catalyst of this invention. When the powder containing the matter containing a functional material, a noble-metals element, or a noble-metals element or a co-catalyst and the powder which made support support these powder are made to put and support on a base material If the catalyst bed formed in the base material front face is made into the thickness of about 5-100 micrometers and the porosity of a catalyst bed is made into 5-50m² / g grade with BET surface area, since catalytic reaction can be kept good, it is desirable.

[0053] In addition, the functional material of this invention cannot be suitably applied in the various field as which oxygen uptake and the emission characteristic are required, and is not limited to application for an oxidation catalyst, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst.

[0054]

[Embodiment of the Invention] A drawing is used for below and the example of this invention is explained to it at a detail. In addition, this invention is not limited to the following examples.

[0055] A carbonic acid cerium (Ce 2(CO 3) 3) and carbonic acid neodymium (Nd 2(CO 3) 3) are used as a start ingredient. (Example 1) Chemical formula: (Nd xCe 1-x) O₂ The functional material with a mean particle diameter of 1 micrometer shown was created with the coprecipitation method so that x might be set to a predetermined value, 0.01 [i.e.,], 0.05, 0.1, 0.15, 0.3, 0.4, 0.5, and 0.8 and 0.9. Let these functional materials be a functional material alpha, a functional material B, a functional material C, a functional material D, a functional material E, a functional material F, a functional material G, a functional material eta, and a functional material I, respectively.

[0056] Next, about the functional material alpha - the functional material I, in order to clarify absorption and the emission characteristic of oxygen, temperature-programmed-desorption (TPD) measurement was performed using isotope oxygen (18O). In addition, in the lock out system which equipped with the cel to which the functional material alpha - the functional material I were set beforehand, TPD measurement performed processing by 18O by the conditions of 300Torr at 600 degrees C for 1 hour, and used the functional material alpha which permuted the oxygen (16O) which exists in the front face and grid of a functional material alpha - a functional material I, and isotope oxygen (18O) - the functional material I. And TPD measurement is 21% of oxygen (nitrogen balance). It carried out circulating Air by the flow rate of 100ml/m.

[0057] As a result of TPD measurement, the activity of TPD had the most expensive functional material F, and, subsequently was expensive. [of the functional material G and the functional material E] Moreover, in the functional material alpha whose value of x is less than 0.1, the

functional material beta, and the functional material C, the activity of TPD was low. The activity of TPD of a functional material D, a functional material H, and a functional material I was mostly located in the middle as the activity of TPD of a functional material E, a functional material F, and a functional material G, and the activity of TPD of a functional material alpha, a functional material beta, and a functional material C, and showed the activity of TPD with three [almost same].

[0058] The oxygen uptake and the emission characteristic of the functional material alpha - functional material I in a 300-600-degree C temperature requirement are shown in drawing 1 .

Oxygen uptake and the emission characteristic had the functional material F as most expensive as 1260micromol/g, and was as the lowest as 420micromol/g so that clearly from drawing 1 . [of the functional material alpha] Moreover, the functional material D was 960micromol/g of a functional material F and a functional material alpha mostly located in the middle.

[0059] The functional material concerning this invention became clear [demonstrating extremely excellent oxygen uptake and the emission characteristic as compared with the conventional cerium oxide represented by a functional material alpha, a functional material beta, and the functional material C] from the above result.

[0060] (Example 2) the functional material alpha created in the example 1, a functional material D, and a functional material F -- respectively -- with a mean particle diameter of 1 micrometer rhod -- electroless deposition -- 10wt(s)% -- every -- it supported and Catalyst A, Catalyst D, and Catalyst F were created.

[0061] Next, about Catalyst A, Catalyst D, and Catalyst F, in order to investigate the engine performance as a methano 1 RU reforming catalyst, the methanol of 99% of purity was supplied, having set Catalyst A, Catalyst D, and Catalyst F to the reactor cel, respectively, and having used reaction temperature as 400 degrees C among atmospheric pressure. Consequently, the invert ratio of methano 1 RU brought a result to which Catalyst alpha followed the oxygen uptake and the emission characteristic with which Catalyst D is 95% and Catalyst F was indicated to be for it in the example 1 81% 69%. The catalyst using the functional material of this invention became clear

[demonstrating the function which was excellent as a methano 1 RU reforming catalyst as compared with the catalyst using the conventional cerium oxide represented by Catalyst alpha] from the above result.

[0062] (Example 3) the functional material F and the platinum with a mean particle diameter of 1 micrometer which were produced in the example 1 -- 1wt% -- after blending the supported graphite dryly by the weight ratio of 1:4 with a mortar, with copper wire, pressurization molding was carried out and the electrode plate of a 10mmx15mm angle was produced.

[0063] Subsequently, an electrode plate is immersed into 1mu sodium-hydroxide water solution in an electrolysis cell, a platinum plate is used for a counter electrode, and bubbling of the carbon monoxide (CO) was carried out to the electrode plate, impressing an electrical potential difference. Then, the current value was 0.15malpha, when the current by oxidation of CO flowed and the overvoltage of 100mV was impressed on normal-hydrogen-electrode criteria.

[0064] on the other hand -- platinum -- 1wt% -- except having produced the electrode plate using the supported graphite, it is the same conditions, and bubbling of the carbon monoxide (CO) was completely carried out to the electrode plate, impressing an electrical potential difference. However, in this case, if the overvoltage of 350mV was not impressed on normal-hydrogen-electrode criteria, the current value of 0.15malpha was not able to be acquired.

[0065] The catalyst using the functional material of this invention made it possible to reduce applied voltage, and became clear [demonstrating the function which was excellent as an electrode catalyst] from the above result.

[0066] (Example 4) It is Pd, using alpha-alpha 1 2O3 [with a mean particle diameter of 1 micrometer] (only hereafter referred to as alphas2O3) as support alphas2O3 It was made to support by electroless deposition upwards, and support with a mean particle diameter of 1.5 micrometers was obtained. In addition, Pd and alphas2O3 A weight ratio is 1:1. Next, the support 50 weight section and the functional material F50 weight section created in the example 1 were often mixed, and the catalyst raw material powder J was obtained. Subsequently, water was added to the catalyst raw material powder J, and the slurry was created. And the dimension applied the slurry to the heat-resistant metal structure base material of the honeycomb configuration which has the gas

passageway of a large number with a diameter [of 30mm], and a flow lay length of 170mm, after desiccation, it calcinated in atmospheric air and the combustion catalyst K was acquired for 900 degrees C and 24 hours.

[0067] On the other hand, as contrast, a functional material F was not added but the combustion catalyst L set up so that the amount of Pd supported on a thermal-protection-system base material might become the same as the combustion catalyst K was produced according to the combustion catalyst K.

[0068] And the coil was filled up with the combustion catalyst K and the combustion catalyst L, respectively, and the trial examination (combustion test) of a gas turbine combustor was performed. In addition, air was supplied by 2 N-m³ / min, and methane was supplied to the coil by the flow rate of 60 N-L/min, respectively. Moreover, the pressure within a reaction was set to 0.7muPa, the temperature of the air supplied to a coil was changed, and the combustion efficiency in a coil outlet was measured.

[0069] Consequently, although temperature required to attain 90% of combustion efficiency was about 400 degrees C when the combustion catalyst K was used, when the combustion catalyst L was used, combustion did not start until it became about 500 degrees C.

[0070] The catalyst using the functional material of this invention made it possible to burn a fuel from a low-temperature region, and became clear [demonstrating the function which was excellent as a combustion catalyst] from the above result.

[0071]

[Effect of the Invention] In the cerium oxide which is expressed with chemical formula: $(A_x Ce_{1-x}) O_2$ (at least one sort of elements chosen from the group which A becomes from Y, Sc, and a lanthanoids among a formula) according to this invention as explained above Since the value of x in the rate, i.e., above-mentioned chemical formula, of Element alpha was specified in the range of $0.1 < x < 1$, the functional material which is excellent in the capacity which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere can be offered.

[0072] Moreover, since the functional material which is excellent in the capacity which absorbs oxygen under an oxidizing atmosphere and emits oxygen under reducing atmosphere is applied according to this invention, catalytic activity is high, it excels also in the durability of catalytic activity, and the oxidation catalyst which attained efficient use of an energy resource and reduction of an environmental pollutant, a combustion catalyst, a methanol reforming catalyst, and an electrode catalyst can be offered.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing having shown the oxygen uptake and the emission characteristic of the functional material alpha - functional material I in a 300-600-degree C temperature requirement.

[Drawing 2] Drawing in which having expanded a part of combustion catalyst 1 typically, and having shown it.

[Drawing 3] Drawing having shown the base material constituted by honeycomb structure.

[Drawing 4] Drawing having shown the calculation approach of the particle size of a particle.

[Description of Notations]

1 Combustion catalyst 2 .. Oxidization palladium 3 .. Functional material

4 Interface 5 .. Interface 6 .. Base material 7 .. Honeycomb wall

8 Particle of the configuration of arbitration 9 .. Virtual particle

[Translation done.]

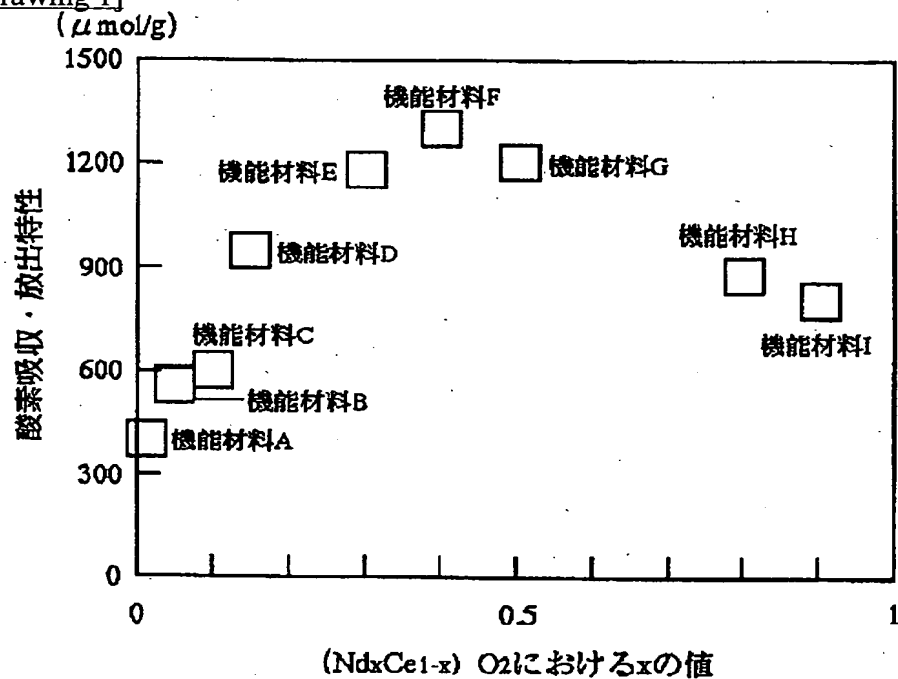
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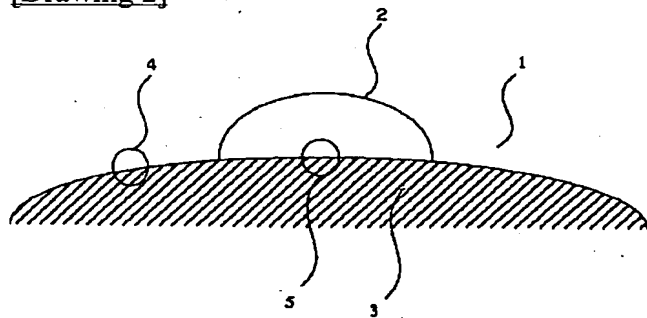
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DRAWINGS

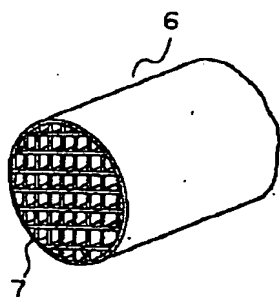
[Drawing 1]



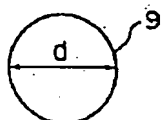
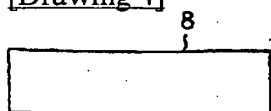
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]

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(54) FUNCTIONAL MATERIAL, OXIDIZING CATALYST, COMBUSTION CATALYST, METHANOL MODIFIED CATALYST AND ELECTRODE CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a functional material of superior function of absorbing oxygen under the oxidizing atmosphere and exhaust oxygen under the reduction atmosphere by using an element of specified value in a cerium oxide represented by the specified formula.

SOLUTION: A function material is represented by the formula of $(A_xCe_{1-x})O_2$ (In the formula, A represents at least one element selected out of a group Y, Sc and lanthanoid, and $0.1 < x < 1$).

The value of X in the formula is set preferably in the range of approximately 0.2-0.7, more preferably approximately 0.3-0.7 (both included). As the particle diameter of the functional material, approximately 0.01-100 μ m is preferred. The functional material of superior capability of absorbing oxygen under the oxidizing atmosphere and existing oxygen under the oxidizing atmosphere can be provided by the above arrangement, and also an oxidizing catalyst, a combustion catalyst, a methanol modified catalyst and an electrode catalyst of high catalyst activities and superior continuity of catalyst activities for achieving the efficient utilization of energy resources and the reduction of generation of environmental pollutants can be provided by the application of the above arrangement.

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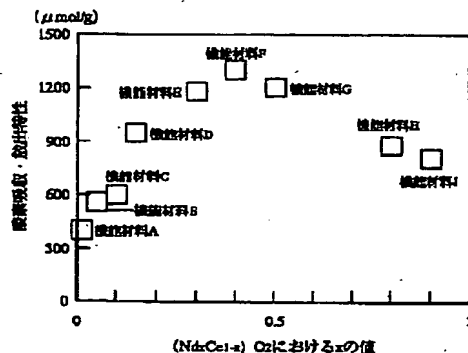
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(54) 【発明の名称】 機能材料、酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒

(57) 【要約】

【課題】 酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力に優れる機能材料と触媒活性が高く、触媒活性の持続性にも優れ、エネルギー資源の効率的な利用と環境汚染物質の低減とを達成する酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒とを提供すること。

【解決手段】 化学式： $(A_xCe_{1-x})O_2$ (式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$) で表される機能材料と、この機能材料を少なくとも具備した触媒による。



【特許請求の範囲】

【請求項1】 化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料。

【請求項2】 化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料を具備したことを特徴とする酸化触媒。

【請求項3】 化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、

貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴とする酸化触媒。

【請求項4】 化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、

貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴とする燃焼触媒。

【請求項5】 化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、

貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴とするメタノール改質触媒。

【請求項6】 化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、

貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴とする電極触媒。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、酸素を吸収する能力に優れるとともに、吸収した酸素を放出する能力にも優れる機能材料と、この機能材料を用いることにより高い触媒活性を実現した酸化触媒、燃焼触媒、メタノールの改質触媒および固体電解質型燃料電池等に用いられる電極触媒に関する。

【0002】

【従来の技術】近年、石油、石炭等の化石燃料に代表されるエネルギー資源の枯渇化や、化石燃料からエネルギーを取り出す際に発生する環境汚染物質の増加が大きな社会問題となっている。すなわち、化石燃料に代表され

るエネルギー資源の枯渇化は、化石燃料に代わる有力なエネルギー源が開発されていない現状では人類の活動に直接影響する。また、環境汚染物質の増加は地球的規模の生態系の破壊をもたらし、人類のみならず種の多様性の存立をも危ういものとしている。したがって、エネルギー資源の枯渇化を抑制し、環境汚染物質の発生を抑制して生態系を維持してゆくことは、今後の地球を占う上から最重要課題となっており、そのためには、エネルギー資源を効率的に利用し、環境汚染物質を低減することが必要不可欠である。

【0003】そこで、上述の要求を満たすために、天然ガスを用いて高効率に発電を行うガスタービン、自動車の排気ガスを清浄化する排ガス浄化触媒、高い転化率で生成物を生成する反応触媒および高い変換効率で電気エネルギーを生成する燃料電池等の手段が急ピッチで開発されている。現在、これらの手段に対しては要求されるスペックに応じて種々の材料が提案されているが、中でもセリウム化合物は、使用環境中での安定度が高く、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出するという特性を有することから、重要な材料として広く用いられている。

【0004】ガスタービンは、メタン等を主成分とする燃料を酸化反応により燃焼させることが主流となりつつあるが、そのために、低温度から酸化反応を開始するパラジウムを触媒成分として用いることが多い。ところで、パラジウムは酸化状態（PdO）のときは触媒活性が高く、金属（Pd）のときは触媒活性が低いという特性を有している。酸化パラジウムは、酸素分圧と雰囲気温度とによって支配される平衡によって900℃以上で酸素を放出して金属（Pd）となる。

【0005】一般に、酸化パラジウムを触媒成分とする燃焼触媒の触媒反応は、触媒表面に酸素が解離吸着したPd-Oの酸化物状態で炭化水素類を酸化し、酸化パラジウム自身は還元されて金属（Pd）となり、金属（Pd）は再び酸化されてPd-Oの酸化物状態を生成し、これを繰り返して炭化水素類を酸化するレドックス反応である。通常の炭化水素類の酸化反応では反応量が多くないためレドックスサイクルが触媒表面上で円滑に進行する。しかし、ガスタービンのように燃焼負荷（酸化反応量）が大きい反応系では、レドックスサイクルのバランスが崩れて触媒表面に解離吸着したPd-Oの酸素が容易に消費されるとともに、燃焼触媒の内側に存在しているバルクの酸化パラジウム（PdO）の酸素が触媒表面に移動して燃料の酸化に使用されていると考えられる。すなわち、酸化反応の初期状態では、燃焼触媒中のパラジウムのほとんどが酸化パラジウムであるため高い触媒活性を呈するが、燃焼反応の進行に伴ってバルクの酸化パラジウム（PdO）の酸素が消費されるため、触媒表面に金属（Pd）の割合が増加し、触媒活性が低下する。そこで、酸化雰囲気下で雰囲気中の酸素を吸収

し、還元雰囲気下で酸素を放出することが可能な酸化セリウムをパラジウムとともに共存させることにより、燃焼触媒の触媒活性を維持することが試みられている。

【0006】また、エンジン性能と燃費を損なうことなく排ガス中の炭化水素、一酸化炭素あるいは窒素酸化物の濃度を低減するために、Pt、PdおよびRhからなる三元触媒が排ガス浄化触媒として用いられているが、この三元触媒に酸化セリウムを添加することが試みられている。すなわち、酸化セリウムの助触媒効果を発揮させることで、三元触媒中の貴金属使用量を低減させるとともに、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出することが可能な酸化セリウムの特性によって、自動車の走行モードに起因する空燃比の揺らぎに対応しようとするものである。

【0007】さらに、メタノールの改質反応に際しては、 $(Nd_xCe_{1-x})O_2$ ($0 \leq x \leq 0.1$) 等を、酸化反応を促進させる反応触媒として利用している。

【0008】また、固体酸化物電解質型燃料電池では、正極触媒として、1000℃の空气中で安定で、空気、電解質の両者と大きい接触を持つ構造の、ペロブスカイト型ランタン系遷移金属酸化物に代表される電子導電性の多孔体が用いられている。

【0009】

【発明が解決しようとする課題】しかしながら、従来のセリウム酸化物やペロブスカイト型ランタン系遷移金属酸化物等では、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力が低いという問題があった。

【0010】また、従来のセリウム酸化物やペロブスカイト型ランタン系遷移金属酸化物等では、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力が十分ではないため、これらを適用した触媒の触媒活性が十分に上がらず、また、触媒活性の持続性にも乏しくなるので、現在、要求されているエネルギー資源の効率的な利用と、環境汚染物質の低減とを達成することが困難であるという問題があった。

【0011】本発明は、上記の問題を解決するためになされたもので、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力に優れた機能材料を提供することを目的とする。

【0012】また、本発明は、触媒活性が高く、触媒活性の持続性にも優れ、エネルギー資源の効率的な利用と環境汚染物質の低減とを達成する酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒を提供することを目的とする。

【0013】

【課題を解決するための手段】本発明者らは、化学式： $(A_xCe_{1-x})O_2$ (式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素) で表されるセリウム酸化物において、元素Aの割合、すなわち上記化学式におけるxの値を0.1より増

加させることによって、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する性能が飛躍的に向上することを見出し、本発明にいたったものである。

【0014】すなわち、本発明に係る機能材料は、化学式： $(A_xCe_{1-x})O_2$ (式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$) で表されることを特徴としている。

【0015】本発明の機能材料においては、電子導電性が高いことから、酸化雰囲気中の酸素は以下の反応によって容易に解離し、機能材料に存在する空孔へ取り込まれると考えられる。

【0016】 $1/2 O_2$ (気相中) + $2 e^-$ (機能材料) $\rightarrow O^{2-}$ (空孔)

一方、還元雰囲気の下では、空孔に取り込まれた酸素(イオン)は、以下の反応によって、容易に機能材料の外部に放出されることが考えられる。

【0017】 O^{2-} (空孔) $\rightarrow 1/2 O_2$ (気相中) + $2 e^-$ (機能材料)

上述したように、本発明の機能材料は電子導電性が高いので、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力に優れると考えられる。本発明の機能材料は、400℃で比抵抗100Ω・cm程度の特性を有している。

【0018】本発明の機能材料において、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する性能を良好に発現させるためには、元素Aの割合、すなわち、上記化学式におけるxの値を0.1~1の範囲(ただし、端点は含まず)に設定すればよい。しかしながら、上記化学式におけるxの値を0.2~0.7、より好ましくは0.3~0.7の範囲(端点を含む)に設定することで、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する性能をより良好に発現させることができる。

【0019】また、本発明に係る機能材料を製造するにあたっては、共沈法を用いて、元素Aをセリア(CeO_2)へドープすることが好ましい。機能材料の粒子の粒径としては、好ましくは0.01~100μm程度であるが、0.1~10μm程度にするとより好ましい。さらに、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する性能を良好に発現させるためには、機能材料の表面積をなるべく大きくし、反応の場を増加させることが望ましい。実用的には、機能材料の表面積が、BET表面積で1~100[m²/g]程度であれば、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する性能を良好に発現させることができる。

【0020】なお、粒子の粒径とは、図4に示すように、二次元的に認識された、任意の形状の機能材料の粒子、例えば8を、二次元的に表される仮想粒子9に換算した際の直径dを指すものとする。すなわち、任意の形

状の機能材料の粒子8の面積を求める。次に、求められた面積と等しい面積を有する円形の仮想粒子9を求め、仮想粒子9の直径dを、機能材料8の粒径とする。上述した機能材料の粒子の粒径は、仮想粒子9から求めた値である。また、平均粒径とは、機能材料の集合体において、各機能材料の粒径をもとにして得られる粒径の平均値に相当する値である。以降、物質の粒径および平均粒径は、上述した定義にしたがって算出した数値によって与えるものとする。

【0021】次に、本発明に係る酸化触媒は、化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料を具備したことを特徴としている。

【0022】また、本発明に係る酸化触媒は、化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴としている。

【0023】さらに、本発明に係る燃焼触媒は、化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴としている。

【0024】また、本発明に係るメタノール改質触媒は、化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴としている。

【0025】さらに、本発明に係る電極触媒は、化学式： $(A_xCe_{1-x})O_2$ （式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素、また、 $0.1 < x < 1$ ）で表される機能材料と、貴金属元素および貴金属元素を含む化合物からなる群より選択された少なくとも1種の物質とを具備したことを特徴としている。

【0026】本発明に係る酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒において、機能材料の特性は、上述した通りである。また、酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒とは、機能材料、貴金属元素または貴金属元素を含む化合物は勿論のこと、機能材料、貴金属元素または貴金属元素を含む化合物と他の添加物との混合物、機能材料、貴金属元素または貴金属元素を含む化合物や前述の混合物を担持した担体、

機能材料、貴金属元素または貴金属元素を含む化合物、前述の混合物あるいは前述の担体を具備した基材をも総称する広範な概念である。

【0027】本発明の酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒は、化学反応に要する酸素を機能物質にとりこみ、反応過程で酸素が欠乏した局面で酸素を放出することで、反応過程における酸素の不足を解消し、常に、化学反応を円滑に進めようとするものである。

【0028】本発明の酸化触媒においては、機能材料を単独で用いてもよいが、酸化反応をより円滑に進行させるために、機能材料と貴金属元素または貴金属元素を含む化合物とを併用することがより好ましい。本発明の酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒において、貴金属元素とは、金、銀および白金族元素（Ru、Rh、Pd、Os、IrおよびPt）を総称するものである。また、貴金属元素を含む化合物とは、例えば、貴金属元素の酸化物のことである。貴金属元素および貴金属元素を含む化合物の粒子の粒径は、好ましくは $0.01 \sim 100 \mu m$ 程度、より好ましくは $0.1 \sim 10 \mu m$ 程度にする。

【0029】機能材料と貴金属元素または貴金属元素を含む化合物との割合をどの程度とするかは触媒系によって相違するが、おおそ以下のように規定される。すなわち、単位時間当たりに、機能材料から貴金属元素に供給される酸素原子の合計量が、化学反応の過程で消費される酸素原子の量よりも多くなる、あるいは同量であるようにすればよい。一般的には、機能材料を機能材料と貴金属元素または貴金属元素を含む化合物からなる全体の $40 \sim 90$ 質量%、より好ましくは、 $50 \sim 75$ 質量%程度に選択され、残りが貴金属元素または貴金属元素を含む化合物となる。

【0030】また、本発明の酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒においては、機能材料や貴金属元素または貴金属元素を含む化合物以外の成分に、助触媒として、ニッケル、マグネシウム、チタン、バナジウム、クロム、マンガン、鉄、コバルト、銅、亜鉛、モリブデン、ランタノイドを含む希土類（スカンジウム、イットリウム、ランタン、セリウム、プラセオジウム、ネオジウム、プロメチウム、サマリウム、ユーロビウム、ガドリウム、テルビウム、ジスプロシウム、ホルミウム、エルビウム、ツリウム、イッテルビウム、ルテニウム）、または、これらの金属の酸化物等を加えてもよい。特に、ニッケルまたはその酸化物を加えた場合には触媒活性の向上が大きい。

【0031】このとき、機能材料、貴金属元素または貴金属元素を含む化合物および助触媒との割合は、触媒系によって適宜設定されるので特に限定はされないが、一般的には、機能材料を機能材料、貴金属元素または貴金属元素を含む化合物および助触媒からなる全体の $40 \sim$

90質量%、より好ましくは、50～75質量%程度に選択し、貴金属元素または貴金属元素を含む化合物を機能材料、貴金属元素および助触媒からなる全体の10～60質量%、より好ましくは、15～40質量%程度に選択する。そして、残りが助触媒となる。また、助触媒の平均粒径は、0.01～100 μ m程度が好ましく、さらに好ましくは0.1～10 μ m程度である。

【0032】また、本発明の酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒においては、機能材料あるいは機能材料と貴金属元素または貴金属元素を含む化合物とを、粒子の形態のまま触媒として用いることも可能であるが、好ましくは、機能材料あるいは機能材料と貴金属元素または貴金属元素を含む化合物の粒子を他の担体に担持させることが好ましい。また、機能材料あるいは機能材料と貴金属元素または貴金属元素を含む化合物とに助触媒を添加した場合においても、これらの粒子を他の担体に担持させることが好ましい。担体は、触媒としての使用に際し、機能材料、貴金属元素または貴金属元素を含む化合物および助触媒が凝集する現象を防止するとともに、自らの内部に形成された細孔によって触媒活性を向上させること等にも貢献しており、また、触媒層を形成した場合には触媒層中に細孔を形成する効果を有する。

【0033】担体を構成する物質としては、酸化物または窒化物あるいは炭化物等のセラミックスが挙げられる。金属を担体とすると、雰囲気中に含まれる酸素と反応して金属担体自体が酸化し、最終的に酸化物担体となる場合があるが、酸化しないものは金属担体として使用可能である。これらの中で、金属酸化物、特に遷移金属元素の酸化物は、機能材料と貴金属元素との間で酸素のやりとりを行って触媒活性を向上させる助力となりうるので好ましい。特に、酸化物の中ではジルコニア(ZrO_2)が望ましく、さらにイットリア(Y_2O_3)による安定化を行った立方晶系ジルコニアが望ましい。また、担体は、上記の物質から選択された2種類以上の混合系でもよい。さらに、本発明に係る機能物質自身を担体として貴金属元素を担持することもでき、他の物質を担体として使用しないことも可能である。

【0034】機能材料を担体に担持する場合、機能材料と担体との割合は特に限定はされないが、一般的には、機能材料を機能材料と担体からなる全体の30～70質量%、より好ましくは、40～60質量%程度に選択し、残りを担体とする。また、機能材料と貴金属元素または貴金属元素を含む化合物とを担体に担持する場合、機能材料、貴金属元素または貴金属元素を含む化合物および担体との割合は、触媒系によって適宜設定されるので特に限定はされないが、一般的には、機能材料を機能材料、貴金属元素または貴金属元素を含む化合物および担体からなる全体の30～60質量%、より好ましくは、40～60質量%程度に選択し、貴金属元素または

貴金属元素を含む化合物を機能材料、貴金属元素または貴金属元素を含む化合物および担体からなる全体の10～30質量%、より好ましくは、15～30質量%程度に選択する。そして、残りを担体とする。さらに、機能材料、貴金属元素または貴金属元素を含む化合物および助触媒を担体に担持する場合、機能材料、貴金属元素または貴金属元素を含む化合物、助触媒および担体の割合は、触媒系によって適宜設定されるので特に限定はされないが、一般的には、機能材料を機能材料、貴金属元素または貴金属元素を含む化合物、助触媒および担体からなる全体の30～60質量%、より好ましくは、40～60質量%程度に選択し、貴金属元素または貴金属元素を含む化合物を機能材料、貴金属元素または貴金属元素を含む化合物、助触媒および担体からなる全体の10～30質量%、より好ましくは、10～20質量%程度に選択する。そして、助触媒を機能材料、貴金属元素または貴金属元素を含む化合物、助触媒および担体からなる全体の5～20質量%、より好ましくは、5～10質量%程度に選択し、残りを担体とする。

【0035】機能材料と貴金属元素、あるいは機能材料、貴金属元素または貴金属元素を含む化合物および助触媒を担体に担持した場合には、機能材料と貴金属元素または貴金属元素を含む化合物、あるいは機能材料と貴金属元素または貴金属元素を含む化合物および助触媒との距離は近接しているほど好ましいが、特に接触している必要はない。機能材料と貴金属元素または貴金属元素を含む化合物、あるいは機能材料と貴金属元素または貴金属元素を含む化合物および助触媒との距離が数nm程度であれば、貴金属元素または貴金属元素を含む化合物に対し機能材料の特性は十分に発揮される。

【0036】機能材料、貴金属元素または貴金属元素を含む化合物または助触媒を担体に担持する方法としては、ミリング法、含浸法、共沈法あるいはスパッタ法等が挙げられる。機能材料、貴金属元素または貴金属元素を含む化合物または助触媒を担体（酸化物または窒化物あるいは炭化物等のセラミックス）に担持させるには、単に両者の粉末を混ぜ合わせるだけでもよいが、機能材料、貴金属元素または貴金属元素を含む化合物または助触媒と耐熱性物質との接触が密になり、接触面積も増えて良好な接触が維持される結果、これらの相互作用が高まることから、ボールミルを用いてミリングするのが好ましい。混合の際、通常、雰囲気条件は特に限定されない。また、含浸法、メッキ法、スパッタ法、共沈法等によっても得ることができる。

【0037】また、機能材料、貴金属元素または貴金属元素を含む化合物または助触媒を担体に担持して粉末とした場合、この粉末の平均粒度を、0.01～100 μ m程度とすることが好ましいが、0.1～10 μ m程度とするとより好ましい。ミリング法によって、機能材料、貴金属元素または貴金属元素を含む化合物または助

触媒を担体に担持して粉末とした場合には、0.01～1μm以下の粒径の1次粒子が凝集し、この程度の大きさの粒径を有する2次粒子を生成していることが好ましい。

【0038】なお、担体に機能材料あるいは機能材料と貴金属元素とを担持する際、助触媒も担持する場合には、担体と、機能材料あるいは機能材料または貴金属元素を含む化合物と貴金属元素との混合時に、助触媒を同時に添加してもよいし、混合した後に改めて添加してもよい。

【0039】上述したように、本発明の酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒は、化学反応に要する酸素を機能物質にとりこみ、反応過程で酸素が欠乏した局面で酸素を放出することで、反応過程における酸素の不足を解消し、常に、化学反応を円滑に進めようとするものである。

【0040】ここで、貴金属元素としてパラジウムを用いた燃焼触媒を例として、触媒反応の過程を説明する。なお、この燃焼触媒は、燃料の燃焼時において、触媒活性の高い金属酸化物である酸化パラジウムから奪われる量に相当する酸素を、酸素イオンの動きやすい機能材料によって気相中から供給して補うことにより、パラジウムの再酸化速度の遅れを解消し、常に触媒活性の高い酸化状態、すなわち酸化パラジウムを維持するものである。すなわち、燃料の燃焼時にレドックスサイクル反応（燃焼）で酸化パラジウムから酸素が奪われると、パラジウムを担持している機能材料の表面で酸素が解離し、機能材料を通じて酸素の欠乏したパラジウムに酸素が供給されるので、パラジウムは常に触媒活性の高い酸化パラジウムの状態に保たれ、長期にわたって触媒活性が維持されるのである。

【0041】図2は、燃焼触媒1の一部を模式的に拡大して示したもので、2は酸化パラジウム、3は酸化パラジウム2を担持し、担体としても機能している機能材料である。4は機能材料3と酸素およびメタン等の可燃性ガスの存在する気相との接触領域である界面、5は酸化パラジウム2と機能材料3との接触領域である界面である。そして、図2に示す界面4、機能材料3の内部、界面5、酸化パラジウム2の4つの領域においては、以下のように反応が進行すると考えられる。

【0042】（界面4）以下の反応により、酸素が気相中より機能材料3の内部にある空孔に取り込まれる。

【0043】 $1/2 O_2$ （気相中） $+ 2 e^-$ （機能材料3） $\rightarrow O^{2-}$ （機能材料3の内部）

（酸化物担体3の内部）機能材料3の内部に界面4から酸素が取り込まれるのに対し、界面5に接した酸化パラジウム2では燃焼反応の進行に伴い酸素の欠乏が顕著となっている。この欠乏が原動力となり、界面4から取り込まれた酸素が酸素イオンとして界面4から界面5に移動する。

【0044】（界面5）酸素の欠乏が顕著となっており、還元状態の（酸化）パラジウム2に対し、以下の反応により機能材料3の内部より酸素イオンが供給される。

【0045】 O^{2-} （機能材料3の内部） $+ Pd$ （（酸化）パラジウム2） $\rightarrow PdO$ （酸化パラジウム2） $+ 2 e^-$ （機能材料3）

PdO が、メタンとの燃焼反応に再び関与する。

【0046】上記4つの領域での反応を介し、気相～機能材料3～還元状態の（酸化）パラジウム2へと酸素の供給が順次行われることにより、酸化パラジウム2の再酸化速度の遅れが解消され、燃焼時の触媒活性に持続性が得られる。

【0047】なお、ここでは、機能材料とともに貴金属元素としてパラジウムを用いた燃焼触媒を例として反応機構を説明したが、本発明に係る酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒においても同様の機構によって反応を触媒するものであり、実施の形態としては、特にこの例に限定されるものではない。

【0048】本発明に係る酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒においては、機能材料、貴金属元素または貴金属元素を含む物質および助触媒は、粉末として利用したり、上述したように担体に担持させた粉末として利用することが可能であるが、必要に応じて、これらの粉末を基材上に被着・担持させることが好ましい。これらの粉末を被着・担持させる基材としては、たとえば、耐熱セラミック製、もしくは耐熱耐酸化金属製の板、パイプ、発泡体、ペレットあるいは開口部が正方形、長方形、三角形あるいは六角形等に仕切られたハニカム等が挙げられる。すなわち、基材は、触媒の使用環境に適合した形状に加工されるが、例えば、自動車排ガス用触媒では、図3に示した基材6のように、通風抵抗をより減少させるために、ハニカム壁7を0.1～0.5mm程度にまで薄くしたハニカム構造に構成される。

【0049】さらに、ガスタービンの燃焼器に用いる場合のように、厳しい熱環境下で使用する場合には、基材にも耐熱性が要求されるので、高温酸化性雰囲気中でも安定性を有する材質、例えば、アルミナ、シリカ、マグネシア、コーラジェライト、ムライト、 α -アルミナ、ジルコニアスピネル、チタニアなどのセラミック、もしくはステンレス鋼、ハステロイ、インコネル、その他の耐熱金属等が挙げられるが、特に厳しい熱環境下で使用する場合には、IN738、Mar-M247、IN939等のNi基耐熱合金や、FSX-414、H5-188、MM509等のCo基耐熱合金を用いることが有効である。

【0050】機能材料、貴金属元素または貴金属元素を含む物質または助触媒を含む粉末や、これらの粉末を担体に担持させた粉末を基材上に被着・担持させるためには、これらの粉末を含むスラリーを作成して基材上に塗

布し、その後焼結することにより行うことができる。また、機能材料、貴金属元素または貴金属元素を含む物質または助触媒を含む粉末や、これらの粉末を担体に担持させた担持体を、基材に対して熔射することによって被着・担持させた場合には、基材とこれらの粉末とが強固に結合するため、高温・高速のガスが流れるような過酷な環境下においても耐摩耗性および耐剥離性に優れた触媒を得ることができるのでより好ましい。基材上に触媒層を形成するための溶射としては、プラズマ溶射法やガス溶射法等、各種の溶射方法を適用することができる。また、熔射によって触媒層を形成した場合には、触媒層の表面積が小さくなる傾向があるので、上述の粉末にグラファイトやポリエステル等の炭素材を添加して混合物とし、基材上にこの混合物を溶射して触媒層を形成した後、触媒層を活性ガス雰囲気中で加熱処理し、炭素材を燃焼させる処理を行うと、触媒層から炭素材が除去される際に触媒層に多数の通路が形成されて触媒層の表面積が増大し、触媒活性が高くなるので好ましい。

【0051】さらに、触媒層と基材との剥離をより抑制するために、触媒層と基材との間にニッケル、コバルト、鉄およびクロムの少なくとも1つの元素を含むボンド層を形成するとより好ましい。このボンド層は緻密であればよく、特に形成方式を限定するものではないが、その密度が実質的にガスが透過しない程度であるように形成すると好ましい。

【0052】また、本発明の酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒において、機能材料、貴金属元素または貴金属元素を含む物質または助触媒を含む粉末や、これらの粉末を担体に担持させた粉末を基材上に被着・担持させた場合には、基材表面に形成された触媒層を5~100 μm 程度の厚さとし、触媒層の気孔率をBET表面積で5~50 m^2/g 程度とすると、触媒反応を良好に保つことができるので好ましい。

【0053】なお、本発明の機能材料は、酸素吸収・放出特性が要求される多方面の分野において適宜適用することができるものであり、酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒への適用に限定されるものではない。

【0054】

【発明の実施の形態】以下に、本発明の実施例を図面を用いて詳細に説明する。なお、本発明は以下の実施例に限定されるものではない。

【0055】(実施例1)炭酸セリウム(Ce 、(CO 、))および炭酸ネオジム(Nd 、(CO 、))を出発材料として、化学式： $(\text{Nd}, \text{Ce}, \dots)_x\text{O}_2$ で示される平均粒径1 μm の機能材料を、 x が所定の値、すなわち、0.01、0.05、0.1、0.15、0.3、0.4、0.5、0.8および0.9となるように共沈法によって作成した。これらの機能材料を、それぞれ、機能材料A、機能材料B、機能材料C、機能材料

D、機能材料E、機能材料F、機能材料G、機能材料Hおよび機能材料Iとする。

【0056】次に、機能材料A~機能材料Iについて、酸素の吸収および放出特性を明らかにするため、同位体酸素(^{18}O)を用いて、昇温脱離(TPD)測定を行った。なお、TPD測定は、予め、機能材料A~機能材料Iのセットされたセルを装着した閉塞系において、600 $^{\circ}\text{C}$ で1時間、300 Torrの条件で ^{18}O による処理を行い、機能材料A~機能材料Iの表面および格子に存在する酸素(^{18}O)と同位体酸素(^{16}O)とを置換した機能材料A~機能材料Iを用いた。そして、TPD測定は、酸素21%(窒素バランス)のAirを毎分100 ml の流量で流通させながら行った。

【0057】TPD測定の結果、TPDの活性は、機能材料Fが最も高く、次いで、機能材料Gと機能材料Eが高かった。また、 x の値が0.1未満である機能材料A、機能材料Bおよび機能材料Cでは、TPDの活性が低かった。機能材料D、機能材料Hおよび機能材料IのTPDの活性は、機能材料E、機能材料Fおよび機能材料GのTPDの活性と、機能材料A、機能材料Bおよび機能材料CのTPDの活性とのほぼ中間に位置し、3つとも、ほぼ同じTPDの活性を示した。

【0058】図1に、300~600 $^{\circ}\text{C}$ の温度範囲における、機能材料A~機能材料Iの酸素吸収・放出特性を示す。図1から明らかなように、酸素吸収・放出特性は、機能材料Fが1260 $\mu\text{mol/g}$ と最も高く、機能材料Aが420 $\mu\text{mol/g}$ と最も低かった。また、機能材料Dは、機能材料Fと機能材料Aとのほぼ中間に位置する960 $\mu\text{mol/g}$ であった。

【0059】以上の結果から、本発明に係る機能材料は、機能材料A、機能材料Bおよび機能材料Cに代表される従来のセリウム酸化物と比較して、極めて優れた酸素吸収・放出特性を発揮することが明らかとなった。

【0060】(実施例2)実施例1で作成された機能材料A、機能材料Dおよび機能材料Fに、それぞれ平均粒径1 μm のPdを無電解メッキによって10wt%ずつ担持して、触媒A、触媒Dおよび触媒Fを作成した。

【0061】次に、触媒A、触媒Dおよび触媒Fについて、メタノール改質触媒としての性能を調べるため、反応器セルにそれぞれ触媒A、触媒Dおよび触媒Fをセットして、大気圧中、反応温度を400 $^{\circ}\text{C}$ として、純度99%のメタノールを供給した。その結果、メタノールの転化率は、触媒Aが69%、触媒Dが81%、触媒Fが95%であり、実施例1で示された酸素吸収・放出特性に従った結果となった。以上の結果から、本発明の機能材料を用いた触媒は、触媒Aに代表される従来のセリウム酸化物を用いた触媒と比較して、メタノール改質触媒として優れた機能を発揮することが明らかとなった。

【0062】(実施例3)実施例1で作製された機能材

料Fと、平均粒径 $1\mu\text{m}$ の白金を $1\text{wt}\%$ 担持した黒鉛とを、乳鉢にて $1:4$ の重量比で乾式混合した後、銅線とともに加圧成型して $10\text{mm}\times 15\text{mm}$ 角の電極板を作製した。

【0063】次いで、電極板を電解セル中の 1M 水酸化ナトリウム水溶液中に浸漬し、対極に白金板を用いて、電圧を印加しながら一酸化炭素(CO)を電極板にバブリングさせた。すると、 CO の酸化による電流が流れ、標準水素電極基準で 100mV の過電圧を印加した時、電流値は 0.15mA であった。

【0064】一方、白金を $1\text{wt}\%$ 担持した黒鉛を用いて電極板を作製した以外は、全く同様の条件で、電圧を印加しながら一酸化炭素(CO)を電極板にバブリングさせた。しかしながら、この場合には、標準水素電極基準で 350mV の過電圧を印加しなければ、 0.15mA の電流値を得ることはできなかった。

【0065】以上の結果から、本発明の機能材料を用いた触媒は、印加電圧を低下させることを可能とし、電極触媒として優れた機能を発揮することが明らかとなった。

【0066】(実施例4) 平均粒径 $1\mu\text{m}$ の $\alpha\text{-Al}_2\text{O}_3$ (以下、単に Al_2O_3 とする)を担体として、 Pd を Al_2O_3 上に無電解メッキによって担持させ、平均粒径 $1.5\mu\text{m}$ の担持体を得た。なお、 Pd と Al_2O_3 との重量比は $1:1$ である。次に、担持体50重量部と、実施例1で作成された機能材料F50重量部とをよく混合し、触媒原料粉末Jを得た。次いで、触媒原料粉末Jに水を加えてスラリーを作成した。そして、外形寸法が直径 30mm 、流れ方向の長さ 170mm の、多数のガス流路を有するハニカム形状の耐熱性金属構造基材へスラリーを塗布し、乾燥後、 900°C 、24時間、大気中で焼成を行って燃焼触媒Kを得た。

【0067】一方、対照として、機能材料Fを加えず、耐熱構造基材上へ担持される Pd 量が燃焼触媒Kと同じとなるように設定された燃焼触媒Lを、燃焼触媒Kに準じて作製した。

【0068】そして、燃焼触媒Kおよび燃焼触媒Lを反応管にそれぞれ充填し、ガスタービン燃焼器の模擬試験(燃焼試験)を行った。なお、反応管へは、空気を $2\text{N}\cdot\text{m}^3/\text{min}$ 、メタンを $60\text{N}\cdot\text{L}/\text{min}$ の流量でそれぞれ

供給した。また、反応管内の圧力を 0.7MPa とし、反応管に供給する空気の温度を変化させて、反応管出口での燃焼効率を測定した。

【0069】その結果、燃焼効率 90% を達成するのに必要な温度は、燃焼触媒Kを用いた場合には約 400°C であったが、燃焼触媒Lを用いた場合には、約 500°C になるまで燃焼が始まらなかった。

【0070】以上の結果から、本発明の機能材料を用いた触媒は、低温域から燃料を燃焼させることを可能とし、燃焼触媒として優れた機能を発揮することが明らかとなった。

【0071】

【発明の効果】以上説明した通り、本発明によれば、化学式： $(\text{A}_x\text{Ce}_{1-x})\text{O}_2$ (式中、AはY、Scおよびランタノイドからなる群より選択された少なくとも1種の元素)で表されるセリウム酸化物において、元素Aの割合、すなわち上記化学式におけるxの値を $0.1 < x < 1$ の範囲に規定したので、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力に優れた機能材料を提供することができる。

【0072】また、本発明によれば、酸化雰囲気下で酸素を吸収し、還元雰囲気下で酸素を放出する能力に優れた機能材料を適用しているので、触媒活性が高く、触媒活性の持続性にも優れ、エネルギー資源の効率的な利用と環境汚染物質の低減とを達成した酸化触媒、燃焼触媒、メタノール改質触媒および電極触媒を提供することができる。

【図面の簡単な説明】

【図1】 $300\sim 600^\circ\text{C}$ の温度範囲における、機能材料A～機能材料Iの酸素吸収・放出特性を示した図。

【図2】燃焼触媒1の一部を模式的に拡大して示した図。

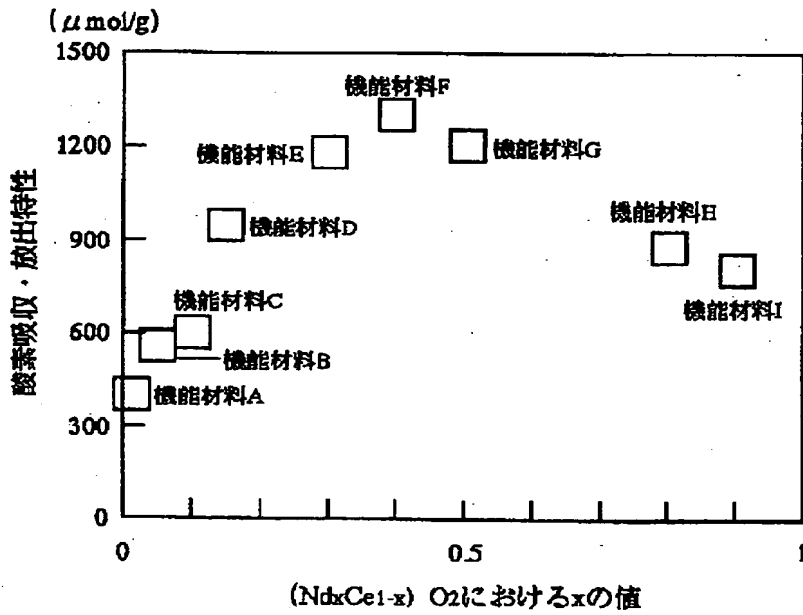
【図3】ハニカム構造に構成された基材を示した図。

【図4】粒子の粒径の算出方法を示した図。

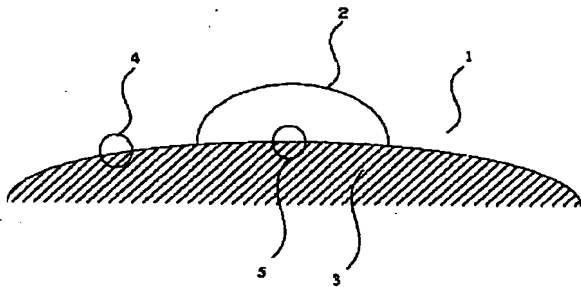
【符号の説明】

1……燃焼触媒 2……酸化パラジウム 3……機能材料
4……界面 5……界面 6……基材 7……ハニカム壁
8……任意の形状の粒子 9……仮想粒子

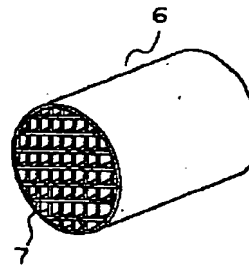
【図1】



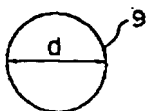
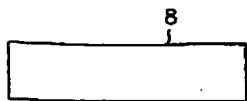
【図2】



【図3】



【図4】



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